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Proton magnetic resonance study of some hexahydrates and tetrahydrates

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Some hexahydrates and tetrahydrates are studied by proton magnetic resonance and it is found, as expected, that the $p-p$ vectors have a definite orientation among them.

1. INTRODUCTION

When a hydrate contains four or six waters of hydration, it may be supposed that these are present as waters of hydration generally arranged *tetrahedrally* or *octahedrally* to the positive ion respectively. (Stillwell 1938). In order to test this hypothesis, a proton magnetic resonance study of these hydrates is helpful. A PMR study of hydrates helps in the determination of the $p-p$ vector orientations. In a tetrahedral or octahedralarray of the waters of hydration (that is to say, the $p-p$ vectors), the vector orientations must have a definite relationship among them. For example, in a regular tetrahedral array, the successive $p-p$ vector orientations must differ by 120°, and in a regular octahedral array, they must be at right angles to each other.

2. TETRAHYDRATES

Three tetrahydrates, $Sr(NO_3)_2.4H_2O$, $BeSO_4.4H_2O$ and $MnSO_4.4H_2O$ were chosen for the study. The third substance $MnSO_4.4H_2O$ could not be used for the PMR study because of its strong paramagnetism though an Electron Paramagnetic Resonance study of it showed that it has its waters of hydration at the ends of a regular tetrahedron since the g-values got by rotation about the b-axis showed isotropy.

The two crystals $Sr(NO_3)_2.4H_2O$ and $BeSO_4.4H_2O$ were grown from solution. Their crystallographic details are shown below :

Strontium nitrate tetrahydrate, $Sr(NO_3)_2.4H_2O$

Monoclinic, White, Prismatic.

Density = 2.249.

a; b; $c = 0.6547 : 1 : 0.8976$.

$\beta = 91° 10'$, $Z = 4$.

Beryllium sulphate tetrahydrate $BeSO_4.4H_2O$

Tetragonal,

$z = 4$,

$a_0 = 8.02$Å $\quad c_0 = 10.75$Å

Space Group : $I4C2$ (V_d^{10}).

Cs Cl-like packing of SO_4 and Be $(H_2O)_4$ tetrahedra).

The salts were studied on a spectrometer constructed in the laboratory for wide-line studies. The details of the experimental study are not given since a good account of the hydrate study by PMR is given in the author's paper on Magnesium thiosulphate hexahydrate $MgS_2O_3.6H_2O$ (Murthy 1963). The following $p-p$ vector orientations were determined :

	θ_1^0	θ_2^0	θ_3^0	θ_4^0
$Sr(NO_3)_2.4H_2O$ (about b axis)	18	138	258	128
$BeSO_4.4H_2O$. (about c_0 axis)	11	131	251	106

The table shows that the successive $p-p$ vectors differ by 120° as is expected for regular tetrahedral arrays.

3. Hexahydrates

One hexahydrate, magnesium thiosulphate hexahydrate, $MgS_2O_3.6H_2O$ has already been studied by the author (Murthy 1963). Now another crystal, nickel thiosulphate hexahydrate, $NiS_2O_3.6H_2O$ was taken up for detailed study.

Nickel thiosulphate hexahydrate $NiS_2O_3.6H_2O$ is isotypic with the Magnesium compound, which has already been studied by the author (Murthy 1963). The crystal structure is hence known through the investigations of Brunt (1946) and later correction by Nardelli *et al* (1962). The PMR study of this compound was also undertaken to investigate, if any, the effects of the paramagnetic ion Ni^{2+} on the location of the proton, as different from the locations in the magnesium compound.

The crystal belongs to the monoclinic class. The tetramolecular unit cell has the following dimensions

$a = 9.39 \pm 1$Å

$b = 14.51 \pm 1$Å

$c = 6.91 \pm 1$Å

$\beta = 90° 41'$

$V = 941$Å^3

Space Group—Pnma.

Since the monoclinic angle is very nearly equal to 90°, the system can be regarded as orthorhombic for all practical purposes without much error. The atomic arrangements are the same as for the Mg-compound. Hence the structure in this compound is also built up of alternating layers of $Ni(H_2O)6$ octahedra and S_2O_3-tetrahedra. The 24 water molecules inside the unit cell fall into three definite groups of eight molecules each so that from the point of view of PMR, we have only three distinct orientations of the $p-p$ vectors.

Preparation of the substance

The nickel thiosulphate hexahydrate crystals were grown by us starting from Sodium thiosulphate (hypo) as in the case of the Mg-compound. First, Barium thiosulphate is got as a white precipitate by mixing saturated solutions of Sodium thiosulphate and Barium Chloride and warming.

$$Na_2S_2O_3 + BaCl_2 \longrightarrow BaS_2O_3 \downarrow + 2NaCl.$$

The solution is filtered and the precipitate collected. To this precipitate is then added a saturated solution of Nickel Sulphate and the mixture is thoroughly shaken and stirred, when Nickel thiosuphate is formed, and being highly soluble, remains in solution. Barium sulphate is left out as a precipitate.

$$BaS_2O_3 + NiSO_4 \longrightarrow NiS_2O_3 + BaSO_4 \downarrow .$$

The solution is filtered off and the green coloured filtrate is slowly evaporated over concentrated sulphuric acid. The green coloured crystals which separate out are exactly similar in appearance to the Mg-thiosulphate crystals except in colour. $NiS_2O_3.6H_2O$ crystals also appear brick-shaped, are long along the c-axis and have clearly cut (011) and (0 $\bar{1}$1) faces at the ends.

Experimental details :

Experiments were done on the NMR Absorption Spectrometer used in the study of the Mg-compound and described earlier (Murthy, 1961, 1962). The crystal used had 1.5 cms. length, 0.7 cms. breadth and 0.45 cms. thickness. The longest side of 1.5 cms. was the c-axis, the side of 0.7 cms. was the b-axis and the side of 0.45 cms. was the crystallographic a-axis.

The crystal was fixed to the crystal head by means of a small quantity of an adhesive cement so that its c-axis was perfectly vertical. The PMR spectra were taken for different orientations of the crystal with respect to the external field direction, starting from the initial position ($\Phi = 0$) of the (100) axis parallel to the magnetic field, and then rotating the crystal in steps of 20° about the vertical axis.

The experiment for each orientation was repeated twice and the average taken to draw the spectra. The experimental conditions are : $\nu_0 = 14.74$ Mc/s.

H = 3473 gauss, Modulation field = 1 gauss, Sweep rate = 1.6 gauss/minute, and Time constant of the p.s.d. = 18 sections. The r.f. level was kept low enough to prevent saturation of the sample. In this case, the r.f. level need not be too low since the paramagnetic ion Ni^{2+} helps relaxation and reduces the relaxation time. In fact, that signals obtained with this salt are stronger than those got with the completely diamagnetic Mg-compound. Rotation about the *b*-axis was not done since the crystal is, for all practical purposes, orthorhombic.

4. Discussion

The spectra obtained are exactly similar to those got for the Mg-compound, though stronger. Hence the analysis of the spectrum is similar to that for the Mg-compound and the Φ, δ, r values also happen to be the same. The Φ_0 and δ values fitting the equation,

$$\Delta H = \frac{3}{2}\frac{\mu^-}{r^3}\{3\cos^2(\Phi+\Phi_0)\cos^2\delta - 1\} \text{ gauss},$$

are :

$\Phi_0^1 = +20°$.	$\delta_1 = 20° 42'$.	$2\alpha_1 = 11.6$ gauss.
$\Phi_0^2 = +110°$.	$\delta_2 = 30° 12'$.	$2\alpha_2 = 12.0$ gauss
$\Phi_0^3 = +97°$.	$\delta_3 = 23° 20'$	$2\alpha_3 = 10.8$ gauss
		Average $2\alpha = 11.5$ gauss

From $2\alpha = 11.5$ gauss, the value of the internuclear distance r is calculated to be 1.51 Å. This small value of r (smaller than the range of values 1.56 to 1.60 Å for the hydrates) can be explained as being due to the presence of a large number of water molecules in a unit cell. It is seen that the Φ_0 values bear approximately a 90° relation among them.

The similarity of the paramagnetic and the diamagnetic PMR spectra of the thiosulphate compounds is due to the fact (which is already recognised in a few cases) that the exchange interaction in the paramagnetic salt narrows the PMR lines since it cancels out the paramagnetic effect. The salt is, for PMR purposes, only diamagnetic. The hydrogen bond scheme and discussion are similar to that given earlier for the Mg-compound.

The experiments were done when the author was in the Indian Institute of Science, Bangalore.

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